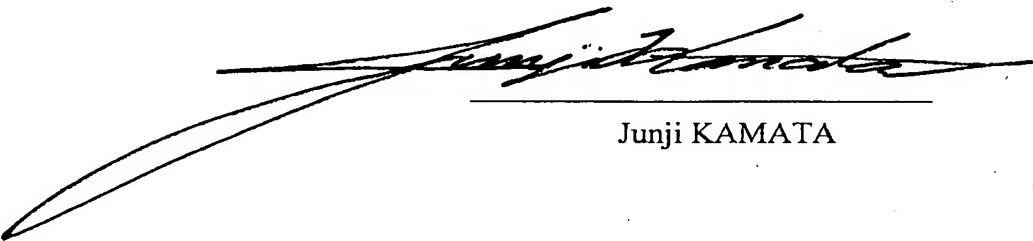


## **DECLARATION**

I, Junji Kamata, Patent Attorney, of SIKs & Co., 8<sup>th</sup> Floor, Kyobashi-Nisshoku Bldg., 8-7, Kyobashi 1-chome, Chuo-ku, Tokyo 104-0031 JAPAN hereby declare that I am the translator of the certified official copy of the documents in respect of an application for a patent filed in Japan on March 31, 2003 under Patent Application No.093738/2003 and that the following is a true and correct translation to the best of my knowledge and belief.

) Dated: November 10, 2006



Junji KAMATA

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Applicant(s) : FUJI PHOTO FILM CO., LTD.

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[Document Name] Description

[Title of the Invention] Gas barrier laminate film and production method therefor as well as substrate and image display device utilizing the film

5 [Claims]

[Claim 1] A gas barrier laminate film comprising a base material film and at least one gas barrier layer obtained by a sol-gel method, wherein a difference between oxygen transmission rate at 25°C in relative humidity of 10% and 10 oxygen transmission rate at 25°C in relative humidity of 90% is within the range of 0 to  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>•day•Pa.

[Claim 2] The gas barrier laminate film according to claim 1, wherein the gas barrier layer is formed by using a polymer having a hydrogen bond-forming group.

15 [Claim 3] The gas barrier laminate film according to claim 1 or 2, wherein the base material film contains a layered compound.

[Claim 4] The gas barrier laminate film according to any one of claims 1-3, which comprises at least one gas barrier 20 layer between at least two base material films.

[Claim 5] A substrate containing the gas barrier laminate film according to any one of claims 1-4.

[Claim 6] An image display device comprising the gas barrier laminate film according to any one of claims 1-4 or the 25 substrate according to claim 5.

[Claim 7] A method for producing a gas barrier laminate film, which comprises applying a solution containing at least one kind of metal alkoxide and a polymer having a hydrogen bond-forming group on a base material film and irradiating the 30 solution with an electromagnetic wave to form a gas barrier layer.

[Claim 8] The method for producing a gas barrier laminate film according to claim 7, wherein the electromagnetic wave is irradiated during a period immediately after completion

of the application of the solution and before completion of drying of the solution.

[Claim 9] The method for producing a gas barrier laminate film according to claim 7 or 8, wherein a microwave is used 5 as the electromagnetic wave.

[Claim 10] A method for producing a gas barrier laminate film, which comprises bonding gas barrier layers of the films, produced by the method according to any one of claims 7-9, to each other to form the gas barrier laminate film.

10 [Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a transparent gas barrier laminate film having both of superior heat 15 resistance and superior gas barrier property, a substrate utilizing the gas barrier laminate film and an image display device such as an organic electroluminescence device (henceforth referred to as an "organic EL device") and liquid crystal display device utilizing the gas barrier 20 laminate film. In particular, the present invention relates to a substrate and image display device utilizing a flexible support.

[0002]

[Prior Art]

25 With the wide spread of personal computers and portable information terminals, the demand for a thin and light electronic display is rapidly increasing. Currently, glass substrates are mainly used in the liquid crystal display devices, which are most widely spread, and in the 30 organic EL devices, which draw attentions because of their high visibility due to the self-coloring property. In view of production of lighter devices, impact resistance, flexibility and so forth, it is preferred that flexible plastic substrates are used as substrates of liquid crystal

devices and organic EL devices. However, plastic substrates have poorer heat resistance and gas barrier property compared with glass substrates. Therefore, they suffer from disadvantages that they are unsuitable for 5 production of highly precise patterns and that their durability is poor.

[0003]

Many researches to improve such drawbacks of plastic substrates have been reported so far. For example, 10 techniques for improving gas barrier property have been reported in the following patent documents.

[0004]

Patent Document 1 discloses an example of use of a plastic substrate having a multilayer structure constituted 15 by layers comprising layered compounds in a liquid crystal display device. This patent document describes that heat resistance, hardness and anti-gas permeability are improved by the use of the layered compounds. However, the gas barrier property described therein cannot be considered sufficient, and further improvement is required. 20

[0005]

Patent Document 2 discloses a laminated film provided with a layer of a composition comprising a layered inorganic compound having a specific aspect ratio and a resin between 25 layers of polyolefin type resin in order to reconcile moisture proofing property and oxygen barrier property.

Patent Document 3 discloses a film having a gas barrier layer comprising a mixture of partial hydrolysate of alkoxide condensate and a water-soluble polymer. However, 30 all of these could not yet provide sufficient oxygen barrier property in high humidity, and the gas barrier property of the whole laminated films needs to be further improved for use in liquid crystal display substrates or organic EL substrates.

[0006]

Further, for improvement of gas barrier property, a method for producing a gas barrier film comprising providing a layer containing a metal alkoxide or a hydrolysate thereof and then irradiating the layer with an electromagnetic wave to produce a gas barrier film. See, for example, Patent Document 4. However, a sufficiently dense film cannot be obtained with a metal alkoxide alone or condensate of metal alkoxide containing a silane coupling agent, and the gas barrier property cannot be considered sufficient for, in particular, use in electronic circuits and display materials.

[0007]

[Patent Document 1] Japanese Patent Laid-open Publication (Kokai) No. 2001-205743 (page 3, [0012] to page 10, [0062])  
[Patent Document 2] Japanese Patent Laid-open Publication No. 7-251489 (page 3, [0005] to page 8, [0034])  
[Patent Document 3] Japanese Patent Laid-open Publication No. 2000-343659 (page 2, [0010] to page 7, [0058])  
[Patent Document 4] Japanese Patent Laid-open Publication No. 2000-313087 (page 3, [0020] to page 4, [0027])

[0008]

[Problems to be solved by the Invention]

The present invention was accomplished in view of the aforementioned problems. The first object of the present invention is to provide a gas barrier laminate film having superior gas barrier property. The second object of the present invention is to provide a highly precise and highly durable substrate and image display device utilizing such a gas barrier laminate film.

[0009]

[Means for solving the Problems]

The inventors of the present invention conducted various researches to obtain favorable gas barrier property

by utilizing characteristics of electromagnetic waves, and as a result, they accomplished the present invention.

That is, the objects of the present invention are achieved by the following gas barrier laminate film, 5 substrate and image display device.

(1) A gas barrier laminate film comprising a base material film and at least one gas barrier layer obtained by a sol-gel method, a difference between oxygen transmission rate at 25°C in relative humidity of 10% and oxygen transmission

10 rate at 25°C in relative humidity of 90% is within the range of 0 to  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>·day·Pa.

(2) The gas barrier laminate film according to (1), wherein the gas barrier layer is an organic/inorganic hybrid layer.

(3) The gas barrier laminate film according to (1) or (2), 15 wherein the base material film is constituted by a polymer having a glass transition temperature of 130 to 300°C.

(4) The gas barrier laminate film according to any one of (1) to (3), wherein the base material film contains a layered compound.

20 (5) The gas barrier laminate film according to any one of (1) to (4), wherein the gas barrier layer is formed by using a polymer having a hydrogen bond-forming group.

(6) The gas barrier laminate film according to any one of (1) to (5), which comprises at least one gas barrier layer 25 between at least two base material films.

(7) A substrate containing the gas barrier laminate film according to any one of (1) to (6).

(8) An image display device comprising the gas barrier laminate film according to any one of (1) to (6) or the 30 substrate according to (7).

[0010]

In the gas barrier laminate film of the present invention, a difference between oxygen transmission rate at 25°C in relative humidity of 10% and oxygen transmission

rate at 25°C in relative humidity of 90% is within the range of 0 to  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>•day•Pa. Since the gas barrier laminate film of the present invention shows superior gas barrier property, in particular, in high humidity, the 5 substrate and image display device utilizing the gas barrier laminate film enable formation of highly precise patterns even in high humidity.

[0011]

10 The objects of the present invention are also achieved by the following production method.

(1) A method for producing a gas barrier laminate film, which comprises applying a solution containing at least one kind of metal alkoxide and a polymer having a hydrogen bond-forming group on a base material film and irradiating the 15 solution with an electromagnetic wave to form a gas barrier layer.

(2) The production method according to (1), wherein the electromagnetic wave is irradiated during a period immediately after completion of the application of the 20 solution and before completion of drying of the solution.

(3) A method for producing a gas barrier laminate film, which comprises bonding gas barrier layers of gas barrier laminate films obtained by the production method according to (1) or (2) to each other to form a gas barrier laminate 25 film.

(4) The production method according to any one of (1) to (3), wherein an alkoxy silane is used as the metal alkoxide.

(5) The production method according to any one of (1) to (4), wherein at least one kind of electromagnetic wave selected 30 from the group consisting of electron rays, ionic rays and low temperature plasmas is used as the electromagnetic wave.

(6) The production method according to any one of (1) to (5), wherein a microwave is used as the electromagnetic wave.

(7) The production method according to any one of (1) to (6),

wherein the electromagnetic wave is irradiated for 5 seconds to 3 minutes immediately after the application of the solution.

[0012]

5 The method for producing a gas barrier laminate film of the present invention comprises applying a solution containing at least one kind of metal alkoxide and a polymer having a hydrogen bond-forming group on a base material film and then irradiating the solution with an electromagnetic  
10 wave. With these steps, the production method of the present invention enables formation of a dense organic/inorganic hybrid layer having superior gas barrier property utilizing characteristics of the electromagnetic wave. In particular, a gas barrier laminate film produced  
15 by the production method of the present invention can exhibit superior gas barrier ability even in high humidity.

[0013]

[Embodiments for carrying out the Invention]

Hereafter, the gas barrier laminate film of the present invention (also referred to as the "laminate film" hereinafter), production method therefor as well as substrate and image display device utilizing the gas barrier laminate film will be explained in more detail.

In the present specification, ranges indicated with "to" mean ranges including the numerical values before and after "to" as the minimum and maximum values.

[0014]

[Laminate film of the present invention]

The laminate film of the present invention has at least one gas barrier layer obtained by a sol-gel method on a base material film.

[0015]

<Base material film>

The base material film used for the laminate film of

the present invention preferably comprises a material having heat resistance so as to be usable for the substrate and image display device described later. It is preferable to use a highly heat-resistant transparent plastic film

5 having a glass transition temperature (Tg) of 100°C or higher and/or a linear thermal expansion coefficient of 40 ppm/°C or lower and/or a light transmittance of 80% or more. Tg and linear thermal expansion coefficient of the base material film can be suitably adjusted by controlling types,

10 contents etc. of additives to be contained in the base material film.

[0016]

The polymer constituting the base material film may be either a thermoplastic polymer or a thermosetting polymer. As for the thermoplastic polymer, preferred is a thermoplastic polymer having Tg of 100 to 400°C, more preferably 130 to 300°C, further preferably 160 to 250°C, as the polymer itself. Further, it is preferably an amorphous polymer in order to obtain optical uniformity.

20 [0017]

Examples of such a thermoplastic polymer as described above include, for example, the followings (abbreviations and Tg are shown in the parentheses): polycarbonate (PC, 140°C), alicyclic polyolefine (e.g., ZEONOA 1600 produced by Nippon Zeon Co., Ltd., 160°C), polyallylate (PAr, 210°C), 25 polyethersulfone (PES, 220°C), polysulfone (PSF, 190°C), cycloolefin copolymer (COC, the compound of Japanese Patent Laid-open Publication No. 2001-150584, Example 1, 162°C), polycarbonate having a modified fluorene ring (BCF-PC, the compound of Japanese Patent Laid-open Publication No. 2000-25

30 227603, Example 4, 225°C), polycarbonate having a modified alicyclic group (IP-PC, compound of Japanese Patent Laid-open Publication No. 2000-227603, Example 5, 205°C), and acryloyl compound (the compound of Japanese Patent Laid-

open Publication No. 2002-80616, Example 1, 300°C or higher). When moisture permeability is desired, it is particularly preferable to use an alicyclic polyolefin and so forth.

5 [0018]

Further, examples of the thermosetting polymer include epoxy type resins and radiation-curing resins. The epoxy type resins include those of polyphenol type, bisphenol type, halogenated bisphenol type and novolak type.

10 As curing agents for curing epoxy type resins, known curing agents can be used. For example, curing agents of amine type, polyaminoamide type, acid and acid anhydride, imidazole, mercaptan and phenol resin can be mentioned. Among these, acid anhydrides, polymers containing an acid 15 anhydride structure and fatty amines are preferably used in view of solvent resistance, optical characteristics, thermal characteristics etc., and acid anhydrides and polymers containing an acid anhydride structure are particularly preferred. Furthermore, a curing catalyst 20 such as known tertiary amines and imidazole derivatives is preferably added in an optimum amount.

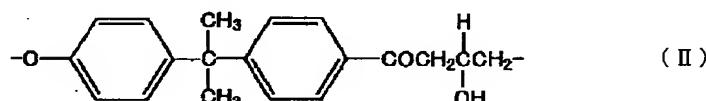
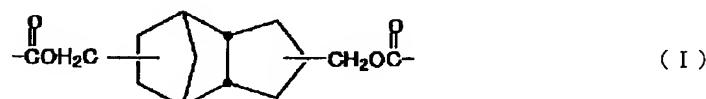
[0019]

The radiation-curing resins are resins of which curing is advanced by irradiation of radiation such as 25 ultraviolet rays and electron rays, more specifically, resins containing an unsaturated double bond such as those of acryloyl group, methacryloyl group and vinyl group in the molecule or a monomer structure. Among these resins, an acrylic type resin containing acryloyl group is 30 particularly preferably used. Although either one kind of radiation-curing resin may be used, or several kinds of the resins may be mixed and used, it is preferable to use an acrylic type resin having two or more acryloyl groups in the molecule or a unit structure. Examples of such a

multi-functional acrylate resin include, for example, urethane acrylate, ester acrylate, epoxy acrylate and so forth. However, it is not limited to these. Acrylate resins containing a unit of the following formula [I] or 5 [II] and having at least two or more acryloyl groups are particularly preferred.

[0020]

[Chemical formula 1]



10

[0021]

When the ultraviolet curing method is used for these radiation-curing resins, a suitable amount of a known photoreaction initiator is added to the aforementioned 15 radiation-curing resins.

[0022]

A hydrolysate of an alkoxy silane or silane coupling agent may be mixed in the aforementioned epoxy type resins and radiation-curing resins in order to further strengthen 20 interactions with polymer molecules. As the silane coupling agent, those having a hydrolyzable reactive group such as methoxy group, ethoxy group and acetoxy group on one hand and having epoxy group, vinyl group, amino group, a halogen group or mercapto group on the other hand are preferred. 25 When such compounds are used, in order to fix them to the main component resin, those having vinyl group having the above reactive group are preferred, and for example, KBM-503 and KBM-803 produced by Shin-Etsu Chemical Co., Ltd., A-187 produced by Nippon Unicar Co., Ltd. and so forth are used.

These are preferably added in an amount of 0.2 to 3 weight %.  
[0023]

The aforementioned base material film may also contain a layered compound. By adding a layered compound to the 5 base material film, a laminated film of which thermal deformation temperature is improved by 2 to 100°C compared with a case where the layered compound is not added is favorably obtained.

[0024]

10 Although the layered compound is not particularly limited, clay minerals, hydrotalcite compounds and other similar compounds having swelling property and/or cleavage property are preferred.

15 Examples of such clay minerals includes kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, beidellite, nontronite, saponite, saucnite, stevensite, hectorite, tetrasylylic mica, sodium taeniolite, muscovite, margarite, talc, vermiculite, phlogopite, xanthophyllite, chlorite and so 20 forth. The aforementioned layered compounds may be either natural substances or synthesized substances. Further, these layered compounds may be used in each kind, or two or more kinds of them may be used together.

[0025]

25 Shape of the aforementioned layered compounds is not particularly limited. However, since cleavage of layered compounds having a lot of layers becomes difficult after organofilization thereof with an organophilizing agent, thickness of the layered compound not organophilized is 30 preferably a thickness of one layer (about 1 nm) as far as possible. The average length thereof is 0.01 to 50  $\mu\text{m}$ , preferably 0.05 to 10  $\mu\text{m}$ , and a layered compound having an aspect ratio of 20 to 500, preferably 50 to 200, can be preferably used.

[0026]

The aforementioned layered compound has ion-exchangeable inorganic cations between layers (including surfaces of uppermost and lowermost layers of inorganic layered compounds). The ion-exchangeable inorganic cations mean metal ions such as those of sodium, potassium and lithium existing on crystal surfaces of the inorganic layered compound (e.g., layered silicate). These ions exhibit a property that they can be exchanged with a cationic substance, and thus various substances having a cationic property can be inserted (intercalated) between the layers of the aforementioned layered compound by an ion exchange reaction.

[0027]

For exchange of inorganic cations existing between layers of the aforementioned layered compound for organic cations, alkylammonium ions containing a long-chain alkyl group are preferably used as the organic cations. Examples of alkylammonium ions containing a long-chain alkyl group include, for example, tetrabutylammonium ion, tetrahexylammonium ion, dihexyldimethylammonium ion, dioctyldimethylammonium ion, hexyltrimethylammonium ion, octyltrimethylammonium ion, dodecyltrimethylammonium ion, hexadecyltrimethylammonium ion, octadecyltrimethylammonium ion, dioctadecyldimethylammonium ion, docosenyltrimethylammonium ion, hexadecyltrimethylammonium ion, tetradecyldimethylbenzylammonium ion, octadecyldimethylbenzylammonium ion, dioleyldimethylammonium ion, polyoxyethylene dodecylmonomethylammonium ion and so forth.

[0028]

Although the cation exchange capacity (CEC) of the aforementioned layered compound is not particularly limited, it is, for example, preferably 25 to 200 meq/100 g, more

preferably 50 to 150 meq/100 g, further preferably 90 to 130 meq/100 g. If the cation exchange capacity of the layered compound is less than 25 meq/100 g, amount of cationic substance that can be inserted (intercalated) 5 between layers of the layered compound by ion exchange becomes small, and the layers may not be sufficiently organophilized. On the other hand, if the cation exchange capacity exceeds 200 meq/100 g, bonding strength between layers of the layered compound becomes too strong. Thus, 10 cleavage of crystal leaves becomes difficult, and dispersibility may be degraded.

[0029]

Examples of the layered compound satisfying the aforementioned requirements include, for example, marketed 15 products such as Sumecton SA produced Kunimine Industries, Kunipia F produced by Kunimine Industries, Somasif ME-100 produced by CO-OP Chemical and Lucentite SWN produced by CO-OP Chemical.

[0030]

As the method for exchanging inorganic cations existing between layers of the aforementioned layered compound for organic cations (organophilization), a wet method is generally used. That is, in the wet method, an inorganic layered compound is sufficiently solvated with 20 water, alcohol or the like, then added with organic cations and stirred so that organic cations should substitute for metal ions existing between layers of the layered compound. Then, unsubstituted organic cations are sufficiently washed off, and the compound is taken by filtration and dried. In 25 addition, it is also possible that the layered compound and organic cations are directly reacted in an organic solvent, or the layered compound and organic cations are reacted by heating and kneading them in the presence of a resin or the like in an extruder.

[0031]

The mixing ratio of the aforementioned layered compound and the polymer having Tg of 100 to 400°C is preferably 1/100 to 100/20, more preferably 5/100 to 100/50, 5 in terms of a weight ratio. If the content of the layered compound is less than 1 part by weight with respect to 100 parts by weight of the polymer having Tg of 100 to 400°C, sufficient heat resistance and gas barrier property may not be obtained. On the other hand, if the content of the 10 polymer having Tg of 100 to 400°C is less than 20 parts by weight with respect to 100 parts by weight of the layered compound, brittleness etc. may be degraded.

[0032]

When a layer containing the layered compound in the 15 polymer having Tg of 100 to 400°C is formed, the layered compound and the polymer having Tg of 100 to 400°C are preferably fusion kneaded or mixed in a solution first to prepare a polymer composition in which the layered compound in a cleaved state is dispersed in the polymer. In view of 20 the production process and cost, they are preferably mixed by the fusion kneading method.

[0033]

As the fusion kneading apparatus usable for the aforementioned fusion kneading, kneading apparatuses 25 generally used for thermoplastic polymers can be used. For example, a single or multi-screw kneading extruder, roller, Banbury mixer and so forth may be used.

[0034]

The aforementioned polymer composition can be made 30 into a film by usual the melt-extruding method, calendering method, solution casting method or the like. Further, the obtained film can also be monoaxially or biaxially stretched.

[0035]

The film surface of the obtained base material film may be subjected to corona discharge treatment, glow discharge treatment, UV treatment, plasma treatment or the like to improve adhesion with the gas barrier layer  
5 described later. An anchor layer may also be provided on the film surface.

[0036]

The laminate film of the present invention is used for image display devices of displays and so forth.

10 Therefore, a transparent base material film, i.e., a base material film having a light transmission of 80% or more, preferably 85% or more, more preferably 90% or more, is preferably used. If the base material film has a light transmission of 80% or more, it can be suitably used as a  
15 base material film of organic EL devices described later.

The light transmission used as an index of transparency in this specification can be measured by the method described in JIS-K7105, i.e., by measuring a total light transmission and scattering light amount using an  
20 integrating sphere type light transmission measurement apparatus and subtracting the scattering light transmission from the total light transmission.

[0037]

<Gas barrier layer>

25 The laminate film of the present invention has at least one gas barrier layer obtained by a sol-gel method on the aforementioned base material film. In the laminate film of the present invention, the gas barrier layer is not particularly limited so long as it is obtained by the sol-  
30 gel method and exhibits favorable gas barrier performance in high humidity. It is preferably an organic/inorganic hybrid layer obtained by the sol-gel method.

[0038]

The "organic/inorganic hybrid" referred to in this

specification means a state that an inorganic substance and an organic substance is mixed at a molecular level and nano order level, and refers to, for example, composite materials of an organic material and inorganic material obtained by  
5 the sol-gel methods described in *Adv. Polym. Sci.*, 100, 11 (1992); *Poly. Mater. Encyclopedia*, 6, 4793 (1996); and *Current Opinion in Solid State & Materials Science*, 1, 806 (1996).

[0039]

10 The aforementioned gas barrier layer can be obtained by allowing an organic material to coexist with an inorganic material during, before or after a reaction of the inorganic material by using the sol-gel method. In the sol-gel method used for manufacture of the laminate film of the present  
15 invention, a metal alkoxide is hydrolyzed and polycondensed preferably in a solution or coated film to obtain a dense thin film. Further, in this operation, a resin (polymer) may also be used together to obtain an organic/inorganic hybrid material.

20 [0040]

(Metal alkoxide)

The metal alkoxide used in the laminate film of the present invention is an inorganic component of the material constituting the gas barrier layer. In view of reactivity, 25 the metal alkoxide is preferably an alkoxy silane. Besides alkoxy silanes, zirconium alkoxides, titanium alkoxides, aluminum alkoxides and so forth are also preferably used. Metal alkoxides may be used in each kind, or two or more kinds of them may be mixed and used.

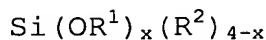
30 [0041]

Alkoxy silanes preferably used in the laminate film of the present invention will be further explained.

Examples of the alkoxy silane include the alkoxy silanes represented by the following formula.

[0042]

[Chemical formula 2]



[0043]

5 In the above formula,  $\text{R}^1$  preferably represents an alkyl group having 1 to 5 carbon atoms or an acyl group having 1 to 4 carbon atoms. Examples include, for example, methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, sec-butyl group, tert-butyl group, acetyl 10 group and so forth.  $\text{R}^2$  preferably represents an organic group having 1 to 10 carbon atoms. Examples include, for example, an unsubstituted hydrocarbon group such as methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, tert-butyl group, n-hexyl group, cyclohexyl 15 group, n-octyl group, tert-octyl group, n-decyl group, phenyl group, vinyl group and allyl group and a substituted hydrocarbon group such as  $\gamma$ -chloropropyl group,  $\text{CF}_3\text{CH}_2-$ ,  $\text{CF}_3\text{CH}_2\text{CH}_2-$ ,  $\text{C}_2\text{F}_5\text{CH}_2\text{CH}_2-$ ,  $\text{C}_3\text{F}_7\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $\text{CF}_3\text{OCH}_2\text{CH}_2\text{CH}_2-$ ,  $\text{C}_2\text{F}_5\text{OCH}_2\text{CH}_2\text{CH}_2-$ ,  $\text{C}_3\text{F}_7\text{OCH}_2\text{CH}_2\text{CH}_2-$ ,  $(\text{CF}_3)_2\text{CHOCH}_2\text{CH}_2\text{CH}_2-$ , 20  $\text{C}_4\text{F}_9\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2-$ , 3-(perfluorocyclohexyloxy)propyl group,  $(\text{CF}_2)_4\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2-$ ,  $\text{H}(\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $\gamma$ -glycidoxypipyl group,  $\gamma$ -mercaptopropyl group, 3,4-epoxycyclohexylethyl group and  $\gamma$ -methacryloyloxypropyl group.  $\text{x}$  is preferably an integer of 2 to 4.

25 [0044]

Specific examples of these alkoxy silanes are described below.

Examples of the compounds where  $\text{x} = 4$  include 30 tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetraisopropoxysilane, tetra-n-butoxysilane, tetraacetoxysilane and so forth.

[0045]

Examples of the compounds where  $\text{x} = 3$  include methyltrimethoxysilane, methyltriethoxysilane,

ethyltrimethoxysilane, ethyltriethoxysilane,  
n-propyltrimethoxysilane, n-propyltriethoxysilane,  
isopropyltrimethoxysilane, isopropyltriethoxysilane,  
 $\gamma$ -chloropropyltrimethoxysilane,  
5  $\gamma$ -chloropropyltriethoxysilane,  
 $\gamma$ -glycidoxypropyltrimethoxysilane,  
 $\gamma$ -glycidoxypropyltriethoxysilane,  
 $\gamma$ -methacryloyloxypropyltrimethoxysilane,  
 $\gamma$ -mercaptopropyltriethoxysilane, phenyltrimethoxysilane,  
10 vinyltriethoxysilane,  
3,4-epoxycyclohexylethyltrimethoxysilane,  
3,4-epoxycyclohexylethyltriethoxysilane,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{C}_2\text{F}_5\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  $\text{C}_2\text{F}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{C}_3\text{F}_7\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ ,  $(\text{CF}_3)_2\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  
15  $\text{C}_4\text{F}_9\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  $\text{H}(\text{CF}_2)_4\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ,  
3-(perfluorocyclohexyloxy)propyltrimethoxysilane and so  
forth.  
[0046]

Examples of the compounds where  $x = 2$  include  
20 dimethyldimethoxysilane, dimethyldiethoxysilane,  
methylphenyldimethoxysilane, diethyldimethoxysilane,  
diethyldiethoxysilane, di-n-propyldimethoxysilane,  
di-n-propyldiethoxysilane, diisopropyldimethoxysilane,  
diisopropyldiethoxysilane, diphenyldimethoxysilane,  
25 divinyldiethoxysilane,  $(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{Si}(\text{OCH}_3)_2$ ,  
 $(\text{C}_3\text{F}_7\text{OCH}_2\text{CH}_2\text{CH}_2)_2\text{Si}(\text{OCH}_3)_2$ ,  $[\text{H}(\text{CF}_2)_6\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2]_2\text{Si}(\text{OCH}_3)_2$ ,  
 $(\text{C}_2\text{F}_5\text{CH}_2\text{CH}_2)_2\text{Si}(\text{OCH}_3)_2$  and so forth.

[0047]

The polymer used in combination for the sol-gel  
30 reaction preferably has a hydrogen bond-forming group.  
Examples of the polymer having a hydrogen bond-forming  
group include polymers having a hydroxyl group and  
derivatives thereof (polyvinyl alcohol, polyvinyl acetal,  
ethylene-vinyl alcohol copolymer, phenol resin, methylol

melamine etc. and derivatives thereof); polymers having a carboxyl group and derivatives thereof (homopolymers or copolymers containing units of a polymerizable unsaturated acid such as poly(meth)acrylic acid, maleic anhydride and 5 itaconic acid, esters of these polymers (homopolymers or copolymers containing units of a vinyl ester such as vinyl acetate, (meth)acrylic acid ester such as methyl methacrylate or the like) etc.); polymers having an ether bond (polyalkylene oxide, polyoxyalkylene glycol, polyvinyl 10 ether, silicon resin etc.); polymers having an amide bond (N-acylated polyoxazoline and polyalkyleneimine having a >N(COR)- bond (in the formula, R represents hydrogen atom, an alkyl group which may be substituted or an aryl group which may be substituted)); polyvinylpyrrolidine having a 15 >NC(O)- bond and derivatives thereof; polyurethane having a urethane bond; polymers having a urea bond and so forth.

[0048]

Hereafter, the reaction conditions for synthesis of materials forming the aforementioned gas barrier layer will 20 be explained.

During the sol-gel reaction, the metal alkoxide is hydrolyzed and polycondensed in water or an organic solvent. For this reaction, it is preferable to use a catalyst. As the catalyst for hydrolysis, acids are generally used. As 25 the acids, inorganic acids or organic acids may be used. Examples of the inorganic acids include hydrochloric acid, hydrogen bromide, hydrogen iodide, sulfuric acid, sulfurous acid, nitric acid, nitrous acid, phosphoric acid, phosphorous acid and so forth. Examples of the organic 30 acids include carboxylic acids (formic acid, acetic acid, propionic acid, butyric acid, succinic acid, cyclohexanecarboxylic acid, octanoic acid, maleic acid, 2-chloropropionic acid, cyanoacetic acid, trifluoroacetic acid, perfluorooctanoic acid, benzoic acid,

pentafluorobenzoic acid, phthalic acid etc.), sulfonic acids (methanesulfonic acid, ethanesulfonic acid, trifluoromethanesulfonic acid, p-toluenesulfonic acid, pentafluorobenzenesulfonic acid etc.), phosphoric acids and phosphonic acids (phosphoric acid dimethyl ester, phenylphosphonic acid etc.), Lewis acids (boron trifluoride etherate, scandium triflate, alkyltitanic acid, aluminic acid etc.), heteropolyacids (phosphomolybdic acid, phosphotungstic acid etc.) and so forth.

10 The amount of the acid used is 0.0001 to 0.05 mol, preferably 0.001 to 0.01 mol, per 1 mol of metal alkoxide (when alkoxy silane and other metal alkoxide are contained, alkoxy silane + other metal alkoxide).

[0049]

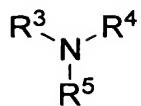
15 After the hydrolysis, basic compounds such as inorganic bases and amines may be added to adjust pH of the solution to make it close to neutral so that condensation polymerization should be promoted.

20 As the inorganic bases, sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, aluminum hydroxide, ammonia and so forth can be used. As the organic base compounds, amines (ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, triethylamine, dibutylamine, 25 N,N-dimethylbenzylamine, tetramethylethylenediamine, piperidine, piperazine, morpholine, ethanolamine, diazabicycloundecene, quinuclidine, aniline, pyridine etc.) and phosphines (triphenylphosphine, trimethylphosphine etc.) can be used.

30 Further, it is also preferable to use, after the hydrolysis with acids, in particular, amines described in Japanese Patent Application No. 2002-110061 and represented by the following formula.

[0050]

[Chemical formula 3]



5 [0051]

In the above formula,  $\text{R}^3$  and  $\text{R}^4$  each independently represent hydrogen atom, an aliphatic group, an acyl group, an aliphatic oxycarbonyl group, an aromatic oxycarbonyl group, an aliphatic sulfonyl group or an aromatic sulfonyl group, and  $\text{R}^5$  represents an aromatic oxy group, an aliphatic thio group, an aromatic thio group, an acyloxy group, an aliphatic oxycarbonyloxy group, an aromatic oxycarbonyloxy group, a substituted amino group, a heterocyclic group or hydroxy group. However, when  $\text{R}^5$  is not an aromatic group, either  $\text{R}^3$  or  $\text{R}^4$  or the both represent hydrogen atom.

In this case, a suitable addition amount of the amine is an equimolar amount to 100 times of the acid in mole, preferably an equimolar amount to 20 times in mole.

20 [0052]

Further, other sol-gel catalysts can also be used in combination. Examples thereof will be shown below.

(1) Metal chelate compounds

Metal chelate compounds having a metal as the center metal and an alcohol represented by the formula  $\text{R}^6\text{OH}$  (wherein  $\text{R}^6$  represents an alkyl group having 1 to 6 carbon atoms) and a diketone represented as  $\text{R}^7\text{COCH}_2\text{COR}^8$  (wherein  $\text{R}^7$  represents an alkyl group having 1 to 6 carbon atoms, and  $\text{R}^8$  represents an alkyl group having 1 to 6 carbon atoms or an alkoxy group having 1 to 16 carbon atoms) as ligands can be suitably used without any particular limitation. Two or more kinds of metal chelate compounds may be used in

combination so long as they are in this category. Those having Al, Ti or Zr as the center metal are particularly preferred as the metal chelate compounds of the present invention. Those selected from a group of compounds 5 represented by the formulas  $Zr(OR^6)_{p1}(R^7COCHCOR^8)_{p2}$ ,  $Ti(OR^6)_{q1}(R^7COCHCOR^8)_{q2}$  and  $Al(OR^6)_{r1}(R^7COCHCOR^8)_{r2}$  are preferred, and they have an action of promoting the condensation reaction.

[0053]

10  $R^6$  and  $R^7$  in the metal chelate compounds may be identical or different, and represent an alkyl group having 1 to 6 carbon atoms, specifically, ethyl group, n-propyl group, isopropyl group, n-butyl group, sec-butyl group, tert-butyl group, n-pentyl group or the like. In addition 15 to the aforementioned alkyl groups having 1 to 6 carbon atoms,  $R^8$  also represents an alkoxy group having 1 to 16 carbon atoms, for example, methoxy group, ethoxy group, n-propoxy group, isopropoxy group, n-butoxy group, sec-butoxy group, tert-butoxy group, lauryl group, stearyl group or 20 the like. In the metal chelate compounds,  $p1$ ,  $p2$ ,  $q1$ ,  $q2$ ,  $r1$  and  $r2$  are integers determined so as to obtain quadridentate or hexadentate ligands.

[0054]

Specific examples of the metal chelate compounds 25 include zirconium chelate compounds such as tri-n-butoxy(ethyl acetoacetate) zirconium, di-n-butoxy•bis(ethyl acetoacetate) zirconium, n-butoxy•tris(ethyl acetoacetate) zirconium, tetrakis(n-propyl acetoacetate) zirconium, tetrakis(acetyl acetoacetate) zirconium and tetrakis(ethyl 30 acetoacetate) zirconium; titanium chelate compounds such as diisopropoxy•bis(ethyl acetoacetate) titanium, diisopropoxy•bis(acetyl acetate) titanium and diisopropoxy•bis(acetylacetone) titanium; aluminum chelate compounds such as diisopropoxy(ethyl acetoacetate) aluminum,

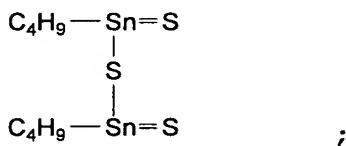
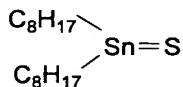
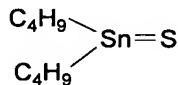
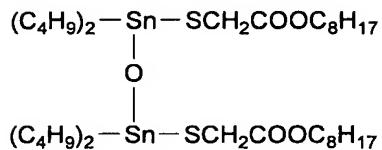
diisopropoxy(acetyl acetonate) aluminum,  
isopropoxy•bis(ethyl acetoacetate) aluminum,  
isopropoxy•bis(acetyl acetonate) aluminum, tris(ethyl  
acetoacetate) aluminum, tris(acetyl acetonate) aluminum and  
5 monoacetyl acetonate•bis(ethyl acetoacetate) aluminum and  
so forth. Among these metal chelate compounds, tri-n-  
butoxy(ethyl acetoacetate) zirconium,  
diisopropoxy•bis(acetyl acetonate) titanium,  
diisopropoxy(ethyl acetoacetate) aluminum and tris(ethyl  
10 acetoacetate) aluminum are preferred. These metal chelate  
compounds can be used in each kind or two or more kinds of  
them can be mixed and used in combination. Further,  
partial hydrolysates of these metal chelate compounds can  
also be used.

15 [0055]

(2) Organic metal compounds

Although preferred organic metal compounds are not  
particularly limited, organic transition metal compounds  
are preferred because of their high activity. Among these,  
20 tin compounds are particularly preferred since their  
stability and activity are favorable. Specific examples of  
these compounds include organic tin compounds including  
carboxylic acid type organic tin compounds such as  
 $(C_4H_9)_2Sn(OCOC_{11}H_{23})_2$ ,  $(C_4H_9)_2Sn(OCOCH=CHCOOC_4H_9)_2$ ,  
25  $(C_8H_{17})_2Sn(OCOC_{11}H_{23})_2$ ,  $(C_8H_{17})_2Sn(OCOCH=CHCOOC_4H_9)_2$  and  
Sn(OCOCC<sub>8</sub>H<sub>17</sub>)<sub>2</sub>; mercaptide type or sulfide type organic tin  
compounds such as  $(C_4H_9)_2Sn(SCH_2COOC_8H_{17})_2$ ,  
 $(C_8H_{17})_2Sn(SCH_2CH_2COOC_8H_{17})_2$ ,  $(C_8H_{17})_2Sn(SCH_2COOC_{12}H_{25})_2$ ,  
[0056]

[Chemical formula 4]



[0057]

5         $(\text{C}_4\text{H}_9)_2\text{SnO}$ ,  $(\text{C}_8\text{H}_{17})_2\text{SnO}$  and reaction products of an organic tin oxide such as  $(\text{C}_4\text{H}_9)_2\text{SnO}$  and  $(\text{C}_8\text{H}_{17})_2\text{SnO}$  and an ester compound such as ethyl silicate, dimethyl maleate, diethyl maleate and dioctyl phthalate, and so forth.

[0058]

(3) Metal salts

10        As the metal salts, alkaline metal salts of organic acids (for example, sodium naphthenate, potassium naphthenate, sodium octanoate, sodium 2-ethylhexanoate, potassium laurate etc.) are preferably used.

[0059]

15        Solvents used in the sol-gel reaction will be explained below. The solvents allow all ingredients in the sol solution to be uniformly mixed, thereby make it possible to prepare solid matter in the composition of the present invention and use it in various coating methods, 20 and improve dispersion stability and storage stability of the composition. These solvents are not particularly

limited so long as they can achieve the aforementioned objects. Preferred examples of the solvents include, for example, water and organic solvents showing high water-miscibility.

5 [0060]

Examples thereof include tetrahydrofuran, dimethoxyethane, formic acid, acetic acid, methyl acetate, alcohols (methanol, ethanol, n-propyl alcohol, isopropyl alcohol, tert-butyl alcohol), ethylene glycol, diethylene glycol, triethylene glycol, ethylene glycol monobutyl ether, acetic acid ethylene glycol monoethyl ether, acetone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide and so forth.

[0061]

15 In order to adjust the sol-gel reaction rate, organic compounds that can constitute multidentate ligands may be added to stabilize the metal alkoxide. Examples thereof include  $\beta$ -diketones and/or  $\beta$ -ketoesters and alkanolamines.

Specific examples of the  $\beta$ -diketones and/or

20  $\beta$ -ketoesters include acetylacetone, methyl acetoacetate, ethyl acetoacetate, n-propyl acetoacetate, isopropyl acetoacetate, n-butyl acetoacetate, sec-butyl acetoacetate, tert-butyl acetoacetate, 2,4-hexanedione, 2,4-heptanedione, 3,5-heptanedione, 2,4-octanedione, 2,4-nonanedione,

25 5-methylhexanedione and so forth. Among these, ethyl acetoacetate and acetylacetone are preferred, and acetylacetone is particularly preferred. One kind of these  $\beta$ -diketones and/or  $\beta$ -ketoesters can solely be used, or two or more kinds of these can be mixed and used in combination.

30 When the aforementioned metal chelate compounds are used as sol-gel catalysts, these compounds that can be multidentate ligands can also be used to adjust the reaction rate.

[0062]

The content of the polymer in the material which constitutes the aforementioned gas barrier layer is 3 to 97 weight %, preferably 5 to 65 weight %, with respect to the weight of the total solid content. Although the addition time of the polymer to the sol-gel reaction system is not particularly limited, it is preferably added until an early stage of the condensation reaction of the metal alkoxide in view of miscibility of them. More preferably, the polymer and the metal alkoxide are mixed before the start of the sol-gel reaction, i.e., before the addition of the acid catalyst.

[0063]

The reaction temperature and time for the synthesis of the material which constitutes the aforementioned gas barrier layer are not particularly limited so long as the reaction system does not become heterogeneous, and they can be suitably adjusted depending on a combination of materials used, hydrolysis ratio of the organic polymer and condensation ratio of the metal alkoxide during the formation of the material which constitutes the desired gas barrier layer and so forth.

[0064]

Hereafter, the gas barrier performance of the laminated film of the present invention will be explained.

In the laminated film of the present invention, a difference between oxygen transmission rate at 25°C in relative humidity of 10% and oxygen transmission rate at 25°C in relative humidity of 90% is within the range of 0 to  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>·day·Pa, preferably 0 to  $1.0 \times 10^{-6}$  ml/m<sup>2</sup>·day·Pa, more preferably 0 to  $5 \times 10^{-7}$  ml/m<sup>2</sup>·day·Pa. If the difference in oxygen transmission rate at 25°C in relative humidity of 10% and 90% is not more than  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>·day·Pa, the oxidation degree of the internal portions are favorably maintained to be constant.

[0065]

<Layer structure>

The laminated film of the present invention has at least one gas barrier layer on a base material film. In the laminated film of the present invention, the thickness of the base material film is preferably 5 to 500  $\mu\text{m}$ , more preferably 5 to 200  $\mu\text{m}$ , further preferably 10 to 100  $\mu\text{m}$ . If the base material film is too thin, the strength becomes insufficient, and handling thereof becomes difficult. If it becomes thicker, transparency tends to be reduced, and flexibility tends to be degraded.

[0066]

In the laminated film of the present invention, the thickness of the gas barrier layer is 0.01 to 10  $\mu\text{m}$ , preferably 0.1 to 10  $\mu\text{m}$ , more preferably 0.1 to 1  $\mu\text{m}$ . If the thickness of the gas barrier layer is 0.01  $\mu\text{m}$  or less, sufficient gas barrier performance may not be obtained. On the other hand, if it becomes thicker than 10  $\mu\text{m}$ , cracks may be generated at the time of drying, and hence the barrier performance may be degraded.

[0067]

The laminated film of the present invention may also have two or more of the aforementioned gas barrier layers. Further, the laminated film of the present invention may have at least one gas barrier layer between at least two of the base material films. By employing a structure where both sides of the gas barrier layer are laminated with base material films, gas barrier performance superior to that of the laminated film having the gas barrier layer on the base material film can be obtained.

[0068]

The laminate film of the present invention may have an inorganic thin film layer between the base material film and the gas barrier layer. As such an inorganic thin film

layer, an inorganic vapor deposition layer of silica, zirconia, alumina or the like is preferred. The inorganic vapor deposition layer can be formed by vacuum vapor deposition, sputtering method or the like.

5 [0069]

The laminated film of the present invention may have, for example, the following layer structures, wherein the base material film is represented by S, the gas barrier layer is represented by B, and the inorganic thin film 10 layer is represented by N. The structure of S/B, wherein the gas barrier layer is provided on the base material film, is more preferred.

[0070]

S/B

15 S/N/B

S/N/B/S

S/B/S/B/S

[0071]

[Production method of the present invention]

20 In the production method of the present invention, a solution containing at least one kind of metal alkoxide and a polymer having a hydrogen bond-forming group is applied on the base material film and then irradiated with an electromagnetic wave to form a gas barrier layer.

25 [0072]

In the production method of the present invention, a solution containing at least one kind of metal alkoxide and a polymer having a hydrogen bond-forming group (hereafter referred to as a "sol solution"), is first applied on a 30 base material film to coat a gas barrier layer by a sol-gel method.

As the metal alkoxide and the polymer having a hydrogen bond-forming group used in the production method of the present invention, those explained for the laminate

film of the present invention can be used.

[0073]

Further, in the production method of the present invention, coating of the material for forming the gas barrier layer can be performed by forming a thin film on the base material film using a coating method such as curtain flow coating, dip coating, spin coating or roll coating. In this case, the time of hydrolysis may be at any time during the production process. For example, there can be suitably used a method in which a solution having a required composition is hydrolyzed and partially condensed to prepare a desired sol solution beforehand, and then it is applied and dried, a method in which a solution having a required composition is prepared and applied and dried while being simultaneously hydrolyzed and partially condensed, a method in which, after a solution is coated and primarily dried, a water-containing solution necessary for hydrolysis is overlaid to attain the hydrolysis, and so forth. Further, various application methods can be used. When productivity is emphasized, a method in which the discharge flow rates of a lower layer coating solution and an upper layer coating solution are adjusted in a slide geeser having multiple discharge ports so that required coating amounts of the solutions should be obtained, and the formed multilayer flows are continuously placed on the base material film and dried (simultaneous multilayer coating method) is preferably used.

[0074]

In the production method of the present invention, the sol solution is applied on the base material film, and then an electromagnetic wave is irradiated on the coated film to form a gas barrier layer.

The electromagnetic wave that is irradiated on the coated film is not particularly limited, and it may be any

of an electron ray, ionic ray and low temperature plasma. If influence on deformation and denaturation of the base material film and well balanced progress of the polycondensation of the metal alkoxide hydrolysate and 5 evaporation of the solvent and byproducts are taken into consideration, a microwave can be particularly preferably used.

[0075]

The microwave to be used is defined as an 10 electromagnetic wave having a frequency of 300 MHz to 300 GHz. Although the microwave used in the present invention may be a microwave having any frequency within the defined range, it is preferably a microwave having a frequency of 1500 MHz to 10 GHz, more preferably 1500 to 3000 MHz, 15 further preferably 2450 MHz.

[0076]

Further, although the output of the microwave used for the present invention can be arbitrarily selected in the range of performance of commercially available 20 apparatuses, a larger output does not necessarily lead to improvement of the gas barrier property or shortening of the film formation time, and it is preferably in the range of 200 to 2000 W, more preferably 200 to 1000 W, most preferably 400 to 800 W. Although the irradiation time may 25 vary depending on the radiation output, it is preferably 10 to 300 seconds, more preferably 10 to 120 seconds, particularly preferably 10 to 60 seconds from economical viewpoint, for the above-defined range of the irradiation output. If the irradiation time is shorter than 10 seconds, 30 the effect of the irradiation markedly decreases. If the irradiation time exceeds 300 seconds, temperature of the film increases, and bad influences are observed such as deformation of the film. Although the microwave may be irradiated intermittently, continuous irradiation is more

preferred. The irradiation temperature can be selected from the range of from room temperature to the deformation temperature of the base material film without any particular limitation, and it is preferably 30 to 150°C, 5 particularly preferably 50 to 130°C.

The irradiation intensity of the microwave is preferably 30 to 500 mJ/cm<sup>2</sup>, more preferably 50 to 400 mJ/cm<sup>2</sup>.

[0077]

10 In the production method of the present invention, the irradiation of the electromagnetic wave is preferably performed during a period immediately after the application of the sol solution on the base material film and before completion of the drying, and the irradiation is more 15 preferably performed immediately after the application. Although the irradiation time is not particularly limited, it is preferably 5 seconds to 10 minutes, more preferably 5 seconds to 3 minutes. By the irradiation of the electromagnetic wave during a step after the application of 20 the sol solution and before the drying, a gas barrier layer having a uniform and dense structure can be obtained. Although the reason for this is not clear at present, it is estimated that if an electromagnetic wave is irradiated on a coated film before drying, temperature rise is caused due 25 to vibration of molecules resulting from polarization at a molecular level, and unreacted portions in which the solvent remains and molecular movements occur at a relatively high level are selectively heated, and water generated by the condensation reaction is selectively heated to promote evaporation thereof, resulting in the 30 formation of the uniform and dense structure.

[0078]

The inventors of the present invention measured solid proton NMR spectra of a gas barrier film formed with

irradiation of a microwave and a gas barrier film produced without irradiation of a microwave. As a result, it was confirmed that the line widths of spectra were broadened by the irradiation of microwave. This indicates that the 5 molecular movements were lowered by the irradiation of microwave and conforms to the aforementioned estimation.

[0079]

In the production method of the present invention, besides the aforementioned microwave, a low temperature 10 plasma, ionic ray and electron ray can be irradiated. This is because irradiation of these can directly give energy for activating the condensation reaction to the reaction sites in which the solvent remains and molecular movements occur at a relatively high level, and thereby the 15 polycondensation of the metal alkoxide hydrolysate becomes likely to advance.

When electron ray irradiation is used with a known electron radiation crosslinkable resin as an organic component, crosslinking of the organic component advances 20 simultaneously with the polycondensation of the metal alkoxide hydrolysate, and thus it becomes easy to obtain a dense film structure in which molecular chains are intertwined with one another. Examples of the electron radiation crosslinkable resin include polyvinyl alcohol, 25 polyoxazoline, polyvinylpyrrolidone and so forth.

Similar effects can also be obtained by ultraviolet irradiation used with a known ultraviolet radiation/electron radiation curing resin and a known photopolymerization initiator as the organic component and 30 electron ray irradiation used with a known ultraviolet radiation/electron radiation curing resin as the organic component. Examples of the ultraviolet radiation/electron radiation curing resin include epoxy acrylate, urethane acrylate, glycerol polyglycidyl ether and so forth.

Examples of the photopolymerization initiator include, for example, benzophenone, diethoxyacetophenone, Sun-Aid SI-100L produced by SanShin Chemical Industry and so forth.

[0080]

5       In the production method of the present invention, at the same time as the irradiation of at least one of the aforementioned electromagnetic wave, electron ray, ionic ray and low temperature plasma and/or after the irradiation, the coated film is desirably subjected to a drying  
10      treatment using a known drying method. Specifically, the hot roll contacting method, heat medium (air, oil) contacting method, infrared heating method and so forth can be mentioned, and the heated air contacting method and infrared drying method are particularly preferred in view  
15      of drying efficiency. Although the temperature for drying is not particularly limited so long as the base material film should not be deformed, it is preferably 150°C or lower, more preferably 30 to 150°C, particularly preferably 50 to 130°C, for the heated air contacting method. When  
20      the infrared drying method is employed, conditions providing a drying surface temperature of 120 to 150°C are preferred.

[0081]

      In the production method of the present invention, 25 gas barrier layers of the obtained gas barrier laminate films can be further bonded to each other to form a gas barrier laminate film. That is, by bonding two of laminate films obtained by the production method of the present invention to each other so that the gas barrier layers 30 should face each other, a laminated film having the base material films outside can be obtained.

[0082]

[Image display device]

      The image display device of the present invention is

a liquid crystal device, organic EL device or the like utilizing the laminate film of the present invention.

The organic EL device having the laminate film of the present invention is preferably used according to, for example, any of the embodiments described in Japanese Patent Laid-open Publication Nos. 11-335661, 11-335368, 2001-192651, 2001-192652, 2001-192653, 2001-335776, 2001-247859, 2001-181616 and 2001-181617, Japanese Patent Application Nos. 2001-58834, 2001-58835, 2001-89663 and 2001-334858.

That is, in an organic EL device having the laminate film of the present invention, the laminate film of the present invention can be used as a base material film and/or a protective film. In the organic EL device of the present invention, the gas barrier film formed by the sol-gel method is preferably coated on the organic EL layer side, i.e., the side that is not brought into contact with outside air.

[0083]

The laminate film of the present invention and the substrate comprising the laminate film are especially useful as electrode substrates of image display devices such as liquid crystal display devices and organic EL devices. In addition, they can also be applied to, for example, electrode substrates also serving as polarizing plates, electrode substrate also serving as phase plates, films with transparent electrodes for touch panels, electromagnetic wave-shielding plates for CRT, plasma display panels (PDP), backlights, light guide panels, color filters, optical guards, optical tapes, optical discs, covers and active devices of solar cells and so forth. Furthermore, they can also be applied to packaging materials for foodstuffs, drugs and so forth.

[0084]

## EXAMPLES

Hereafter, the laminate film of the present invention, production method therefor, substrate and image display device comprising the laminate film will be further 5 explained in detail.

The materials, amounts, ratios, types and procedures of treatments and so forth shown in the following examples can be suitably changed unless such changes depart from the spirit of the present invention. Accordingly, the scope of 10 the present invention should not be construed as limited to the following specific examples.

[0085]

(Example 1)

### 1. Preparation of resin layer (base material film)

ZEONOA 1600R (Tg: 163°C, cycloolefin polymer produced by Nippon Zeon) was mixed per 100 parts by weight with 10 parts by weight of Somasif MTE (synthetic mica produced by CO-OP CHEMICAL), then kneaded and extruded at 270°C by using a double screw extruder (Rheomix 600P/PTW25, HAAKE, 20 Germany) to obtain Resin layer 1A having a thickness of 200 µm. In the same manner as described above except that the content of Somasif MTE was changed as shown in Table 1, Resin layers 1B and 1C were prepared. A resin layer not containing Somasif MTE was also prepared as Resin layer 1D.

[0086]

### 2. Preparation of gas barrier layer

In an amount of 8 g of SOARNOL D2908 (ethylene/vinyl alcohol copolymer produced by Nippon Synthetic Chemical Industry) was dissolved in a mixed solvent of 118.8 g of 1-propanol and 73.2 g of water at 80°C. In an amount of 30 10.72 g of this solution was added and mixed with 2.4 ml of 2 mol/L hydrochloric acid. This solution was added dropwise with 1 g of tetraethoxysilane with stirring and further stirred for 30 minutes. Then, the obtained

application solution was added with dimethylbenzylamine as a pH modifier immediately before application and applied to Resin layers 1A to 1D mentioned above by using a wire bar.

Immediately after the application, each coated layer 5 was irradiated with a microwave of 500 W and 2450 MHz using a microwave generating apparatus with the conditions shown in Table 2 and dried at 120°C for 5 minutes to form a gas barrier layer having a thickness of about 1 μm on each of Resin layers 1A to 1D mentioned above. These are 10 designated Films 2Aa, 2Ab, 2B, 2C, 2Da and 2Db.

Further, instead of the microwave used for Film 2Db, an electron ray with an acceleration energy of 30 keV was irradiated for 0.5 second on the whole surface of the film by using a low energy EB apparatus to produce Film 2E.

15 Further, for comparison, Films 2F to 2I not irradiated with a microwave after coating and Films 2Ac and 2Dc irradiated with a microwave for 60 seconds after drying under the aforementioned conditions, not immediately after the application, were also prepared.

20 Further, PVA is applied on Resin layer 1D instead of the sol-gel layer in the same thickness to prepare Film 2J.

[0087]

### 3. Bonding of films

25 The gas barrier layers of Films 2Ab, 2B, 2C, 2Db and 2I, on which gas barrier layers were formed as described above, were bonded by lamination to produce Films 3Ab, 3B, 3C, 3Db and 3I, respectively.

30 As comparative examples, two of Films 1A, two of Films 2F, two of Films 2Ac, and two of Films 2Dc were bonded to each other, respectively, to produce gas barrier films, and designated Films 3K, 3F, 3Ac and 3Dc, respectively.

[0088]

<Test Example 1>

Heat resistance test (measurement of Tg)

Tg of Resin layer 2Aa, among the resin layers produced as base material films, was measured by the dynamic tension viscoelasticity test method. As a result, 5 Tg of Resin layer Aa was 168°C. From this result, it can be seen that Tg of the resin layer containing the inorganic layered silicate (Resin layer 2Aa) among the resin layers used for the present invention was increased compared with the resin layer not containing the inorganic layered 10 silicate (Resin layer 1Da, Tg: 163°C), and thus heat resistance was improved.

That is, it was found that a resin layer prepared by adding an organic layered silicate to a resin having a high Tg was effective for obtaining higher heat resistance.

15 [0089]

<Test Example 2>

Measurement of gas barrier property

The gas transmission rates of Films 2Aa to 3I were measured at 25°C under atmospheres of relative humidities 20 of 10% and 90% for 24 hours by using PERMATRAN W1A produced by MOCON, and a difference of them was calculated. The results are shown in Table 1.

[Table 1]

Film	Somasif MET content (per 100 weight parts of resin)	Type of irradiated ray	Irradiation condition	Bonding	Difference of oxygen transmission rates at 10% and 90% RH ( $10^{-5}$ ml/m <sup>2</sup> ·day·Pa)	Note
2Aa	10 parts by weight	Microwave	10 seconds immediately after application	None	0.04	Invention
2Ab	10 parts by weight	Microwave	60 seconds immediately after application	None	0.03	Invention
2Ac	10 parts by weight	Microwave	60 seconds immediately before completion of drying	None	0.90	Invention
2B	20 parts by weight	Microwave	10 seconds immediately after application	None	0.64	Invention
2C	30 parts by weight	Microwave	10 seconds immediately after application	None	0.63	Invention
2Da	None	Microwave	10 seconds immediately after application	None	0.88	Invention
2Db	None	Microwave	60 seconds immediately after application	None	0.80	Invention
2Dc	None	Microwave	60 seconds immediately before completion of drying	None	0.96	Invention
2E	None	Electron ray	0.5 second immediately after application	None	0.51	Invention
2F	10 parts by weight	None	—	None	102	Comparative
2G	20 parts by weight	None	—	None	95	Comparative
2H	30 parts by weight	None	—	None	89	Comparative
2I	None	None	—	None	120	Comparative

2J	None	Microwave	0.5 second immediately after application	None		320		Comparative
3Ab	10 parts by weight	Microwave	60 seconds immediately after application	Bonded	0.08			Invention
3Ac	10 parts by weight	Microwave	60 seconds immediately before completion of drying	Bonded	0.98			Invention
3B	20 parts by weight	Microwave	10 seconds immediately after application	Bonded	0.08			Invention
3C	30 parts by weight	Microwave	10 seconds immediately after application	Bonded	0.08			Invention
3Db	None	Microwave	10 seconds immediately after application	Bonded	0.09			Invention
3Dc	None	Microwave	60 seconds immediately before completion of drying	Bonded	0.99			Invention
3F	10 parts by weight	None	—	Bonded	24			Comparative
3I	None	None	—	Bonded	74			Comparative
3K	10 parts by weight	—	—	Bonded	283			Comparative

[0091]

As seen from the results shown in Table 1, all of the gas barrier laminate films produced by the production method of the present invention showed a difference of 5 oxygen transmission rates at relative humidities of 10% and 90% smaller than  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>•day•Pa. Further, when a microwave or electron ray was irradiated during a period immediately after application of an application solution on a base material and before completion of drying, a further 10 smaller difference in oxygen transmission rate was obtained. As for the time of the irradiation, irradiation immediately after the application provided a smaller difference in oxygen transmission rate compared with irradiation immediately before completion of the drying. Furthermore, 15 as for the irradiation time of electromagnetic wave, irradiation of 60 seconds provided more favorable difference in oxygen transmission rate compared with irradiation of 10 seconds.

Further, when the sol solution was coated on the base 20 material film, the difference in oxygen transmission rate was markedly reduced compared with the case where the PVA solution was coated.

From the above results, it can be seen that all of 25 the gas barrier laminate films produced by the production method of the present invention showed favorable gas barrier performance even in high humidity (difference of oxygen transmission rates at relative humidities of 10% and 90% is  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>•day•Pa or less).

[0092]

30 (Example 2)

Production of substrate and organic EL device

Film 3Ab was introduced into a vacuum chamber, and a transparent electrode composed of an ITO thin film having a thickness of 0.2 μm was formed by DC magnetron sputtering

using an ITO target. An aluminum lead wire was connected to the transparent electrode (ITO) to form a laminated structure.

An aqueous dispersion of polyethylene dioxythiophene/polystyrenesulfonic acid (Baytron P, BAYER, solid content: 1.3 weight %) was applied on the surface of the transparent electrode by spin coating and vacuum-dried at 150°C for 2 hours to form a hole transporting organic thin film layer having a thickness of 100 nm. This was 10 designated Substrate X.

[0093]

Further, a coating solution for light-emitting organic thin film layer having the following composition was applied on one side of a temporary support made of 15 polyethersulfone having a thickness of 188 µm (SUMILITE FS-1300, Sumitomo Bakelite) by using a spin coater and dried at room temperature to form a light-emitting organic thin film layer having a thickness of 13 nm on the temporary support. This was designated Transfer Material Y.

20 [0094]

Polyvinyl carbazole (Mw = 63000, Aldrich)	40 parts by weight
Tris(2-phenylpyridine) iridium complex (Ortho-metallated complex)	1 part by weight
Dichloroethane	3200 parts by weight

[0095]

The light-emitting organic thin film layer side of Transfer Material Y was overlaid on the upper surface of the organic thin film layer of Substrate X mentioned above, 30 heated and pressurized at 160°C, 0.3 MPa and 0.05 m/min by using a pair of heat rollers, and the temporary support was delaminated to form a light-emitting organic thin film layer on the upper surface of Substrate X. This was designated Substrate XY.

[0096]

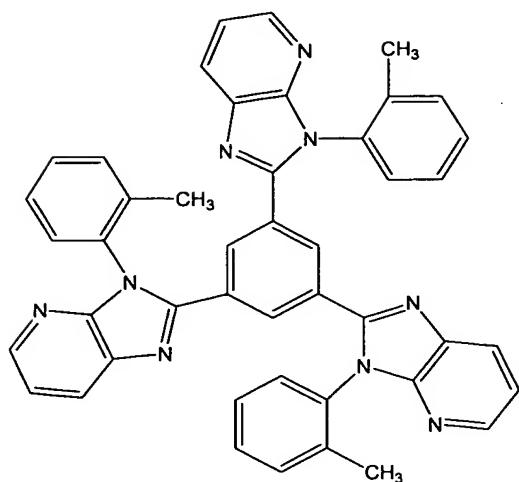
Further, a patterned mask for vapor deposition (mask providing a light-emitting area of 5 mm x 5 mm) was set on one side of a polyimide film (UPILEX-50S, Ube Industries) 5 cut into a 25-mm square and having a thickness of 50  $\mu\text{m}$ , and Al was vapor-deposited in a reduced pressure atmosphere of about 0.1 mPa to form an electrode having a film thickness of 0.3  $\mu\text{m}$ . An aluminum lead wire was connected to the Al electrode to form a laminated structure. A 10 coating solution for an electron transporting organic thin film layer having the following composition was applied on the obtained laminated structure by using a spin coater and vacuum-dried at 80°C for 2 hours to form an electron transporting organic thin film layer having a thickness of 15 nm on LiF. This was designated Substrate Z.

[0097]

Polyvinyl butyral	10 parts by weight
(Mw = 2000, 2000L produced by	
Denki Kagaku Kogyo)	
20 Electron transporting compound	
having the following structure	20 parts by weight

[0098]

[Chemical formula 5]



5 [0099]

1-Butanol

3500 parts by weight

[0100]

Substrate XY and Substrate Z were stacked so that the electrodes should face each other via the light-emitting organic thin film layer between them, heated and pressurized at 160°C, 0.3 MPa and 0.05 m/min by using a pair of heat rollers to obtain Organic EL Device 1.

As comparative organic EL devices, Organic EL Devices 2 and 3 was obtained in the same manner as that described above except that Films 3Ac and 3F were used respectively as the base material film instead of Film 3Ab in the production of Substrate X.

[0101]

DC voltage was applied to the obtained Organic EL Devices 1 to 3 by using Source-Measure Unit Type 2400 (Toyo Corporation) to allow them to emit light. Both of Organic EL Devices 1 and 2 favorably emitted light. After the production of Organic EL devices 1 and 2, they were left at 40°C and relative humidity of 90% for 10 days, and similarly applied with DC voltage. As a result, Organic EL

device 1 similarly showed favorable light emission, whereas defect portions for light emission increased in Organic EL devices 2 and 3.

[0102]

5 Effects of low temperature plasma treatment and ion ray irradiation treatment were similarly examined. As a result, it was confirmed that they had similar effects.

[0103]

[Advantageous effects of the invention]

10 As explained above, the gas barrier laminate film of the present invention has extremely high gas barrier ability represented by a difference in oxygen transmission rate of 0 to  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>•day•Pa at 25°C in relative humidity of 10% and 90%. Therefore, the gas barrier  
15 laminate film of the present invention shows superior gas barrier property even in high humidity. Further, a substrate and image display device utilizing the gas barrier laminate film of the present invention show superior gas barrier property even in high humidity, and  
20 therefore they show high precision and high durability.

[0104]

Further, in the production method of the present invention, hydrolysate of at least one kind of metal alkoxide and a hydrophilic resin are applied, and an  
25 electromagnetic wave is irradiated on the coated film after the formation of the coated film, preferably during a period immediately after the application and before completion of drying, to form a gas barrier layer. By these steps, the production method of the present invention  
30 can provide a dense gas barrier laminate film having superior gas barrier property.

[Document Name] Abstract

[Abstract]

[Object] To provide a gas barrier laminate film showing superior gas barrier property and to provide substrates and image display devices utilizing the gas barrier laminate film with high precision and high durability.

[Solving means] A gas barrier laminate film comprising a base material film and at least one gas barrier layer obtained by a sol-gel method, wherein a difference between oxygen transmission rate at 25°C in relative humidity of 10% and oxygen transmission rate at 25°C in relative humidity of 90% is within the range of 0 to  $1.0 \times 10^{-5}$  ml/m<sup>2</sup>·day·Pa; and a method for producing a gas barrier laminate film, which comprises applying a solution containing at least one kind of metal alkoxide and a polymer having a hydrogen bond-forming group on a base material film and irradiating the solution with an electromagnetic wave to form a gas barrier layer.

[Selected Drawing] No